



## PATENT SPECIFICATION

NO DRAWINGS

*Inventor:* WALTER HOHMANN*Date of Application and filing Complete Specification:* May 21, 1965.*No.* 21628/65.*Application made in Germany (No. F42969 IVc/22b) on May 23, 1964.**Complete Specification Published:* Oct. 18, 1967.

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**Index at acceptance:**—C4 P(Q2K4A, Q2K4B, Q2L3, Q2N1A, Q2N1B, Q4A2, Q4A4, Q4C)**Int. Cl.:**—C 09 b 1/48, C 09 b 5/28

## COMPLETE SPECIFICATION

## New Vat Dyestuffs

We, FARBENFABRIKEN BAYER AKTIENGESellschaft, a body corporate organised under the laws of Germany, of Leverkusen, Germany, do hereby declare the invention, for which we

5 pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 The present invention is concerned with new 1,4,5 - triacylamino -  $\alpha,\alpha'$  - anthrimides and their corresponding 1,4,5 - triacyl carbazolisation products and with the production of said new compounds.

15 We have found that new dyestuffs of the anthraquinone series, giving full and very fast dyeings, are obtained when 1,4,5-triacylamino-8 - chloro - anthraquinones are reacted with amines of the anthraquinone series to form the corresponding anthrimides which are, if

20 desired, condensed in known manner with condensing agents to form anthraquinone-carbazoles.

25 The previously unknown 1,4,5 - triacylamino - 8 - chloro - anthraquinones can be obtained by acylation of the 1,4,5 - triamino-8 - chloro - anthraquinone upon which they are based, and this in turn is obtainable from 1,4 - diamino - 5,8 - dichloro - anthraquinone by the exchange of one halogen atom

30 for an amino group by known methods, for example, *via* the corresponding *p*-toluenesulphamino compound. The 1,4,5 - triacylamino - 8 - chloro - anthraquinones contain as acyl radicals preferably benzoyl radicals which may be substituted. The benzoyl

35 radicals may contain vatable systems as substituents, for example. These compounds can be obtained in that the corresponding triamino-chloro-anthraquinones are reacted by

40 heating with suitable acylating agents, for example, benzoyl chloride, anthraquinone-2-carboxylic acid chloride or thiazole-anthrone-2-carboxylic acid chloride. The triacylamino

compounds used for the process according to the present invention may also contain various aroyl radicals which can be obtained, for example, by the successive reaction of the triamino compounds with various acylating agents. The reaction is preferably carried out in a solvent, such as nitrobenzene.

50 Examples of amines of the anthraquinone series with which the reaction according to the present invention can be carried out are 1 - amino - anthraquinone, 1,4-, 1,5- and 1,8-diamino- or -amino-benzoylamino-anthraquinones, amino- or diamino-1,1'-dianthrimides and those anthraquinones which contain heterocyclic rings besides a free amino group, such as amino-anthraquinone-benzacridone or amino-anthra-pyrimidines.

60 The reaction of the triacylamino-8-chloro-anthraquinones with the amino-anthraquinones to form anthrimides can be carried out by prolonged boiling of the components in high-boiling organic solvents, such as nitrobenzene, naphthalene or technical alkyl - naphthalene mixtures, with the addition of acid-binding agents, such as tertiary bases, alkali metal or alkaline earth metal carbonates or acetates, and preferably in the presence of catalysts, such as copper salts.

70 The resultant reaction products, some of which are themselves dyestuffs, can be treated with carbazolisating condensing agents, such as aluminium chloride, by themselves or in combination with sodium chloride, tertiary organic bases, ammonia or sulphurous acid. The carbazolisation may be carried out in the usual manner known for this reaction by the art.

80 The new compounds according to the present invention are valuable dyestuffs. They can be used, for example, for dyeing and printing vegetable fibres. The dyeings and prints produced with them have great colour strength and are very fast.

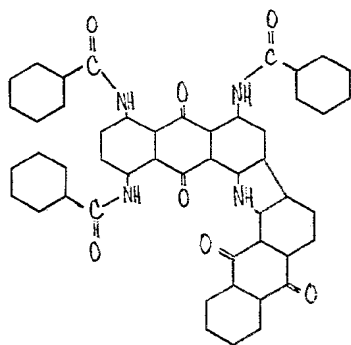
85 The following Examples are given for the

purpose of illustrating the present invention, the parts being parts by weight, unless otherwise stated.

#### EXAMPLE 1

(a) 20 Parts 1,4,5 - tribenzoylamino - 8 - chloro - anthraquinone, 9 parts 1 - amino - anthraquinone, 3.3 parts sodium carbonate, 2 parts copper mixture and 200 parts naphthalene are heated together for 5 hours until the naphthalene reaches boiling point. The mixture is then allowed to cool to 130° C, diluted with 200 parts chlorobenzene, the precipitated product is filtered off with suction at 80° C, washed with chlorobenzene and freed from adherent solvent and the salts by steam distillation. 24 Parts 4,5,8 - tribenzoylamino - 1,1' - dianthrimide are obtained. This compound dissolves in concentrated sulphuric acid with a green colour. The colour of the flakes in water is grey-blue.

(b) 10 Parts of this compound are introduced at 110° C into a melt of 40 parts aluminium chloride and 90 parts pyridine, the melt is heated to 140° C, while distilling off part of the pyridine, and kept at the same temperature for one hour. The melt is poured into a dilute sodium hydroxide solution and heated to 80° C, while adding some sodium hypochlorite. After filtering and drying, there are obtained 10 parts of a dyestuff which dyes cotton from a red-brown vat in full grey shades. Its constitution corresponds to the following structural formula:



#### EXAMPLE 2

(a) 45 Parts 1,4,5-tribenzoylamino-8-chloro-anthraquinone, 27 parts 1-benzoylamino-4-amino-anthraquinone, 8.5 parts sodium carbonate, 1 part copper powder and 450 parts nitrobenzene are heated together at 215° C for 6 hours. The melt is then steam distilled until the nitrobenzene is completely removed. The mixture is then boiled with dilute hydrochloric acid, the anthrimide is isolated by filtration, washed until neutral and dried.

(b) When the product thus obtained is treated with aluminium trichloride-pyridine as described in Example 1 (b), a dyestuff is obtained, which dyes cotton from a brown vat in black-brown shades. Its structure corresponds to that of a bis-phthalylcarbazole which

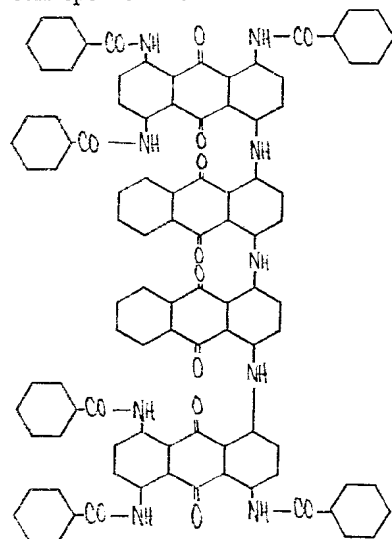
contains one more benzoylamino group than shown in the formula of Example 1.

#### EXAMPLE 3

When, in Example 2, an equal amount of 1 - benzoylamino - 5 - amino - anthraquinone is used, instead of 27 parts 1 - benzoylamino - 4 - amino - anthraquinone, an isomeric dianthrimide is obtained which, when treated with aluminium trichloride, pyridine, yields a vat dyestuff which dyes cotton in grey-brown shades.

#### EXAMPLE 4

(a) 72 Parts 1,5,8 - tribenzoylamino - 4 - chloro - anthraquinone, 25 parts 4,4'-diamino-1,1'-dianthrimide, 9 parts potassium carbonate, 4 parts sodium acetate, 2 parts copper acetate, 1 part cuprous chloride and 1 part copper powder are heated under reflux in 1000 parts naphthalene for 12 hours. When the reaction is completed, the mixture is diluted with 1000 parts chlorobenzene, starting at 140° C. The product is filtered off with suction at 100° C, washed thoroughly with hot chlorobenzene, freed from the solvent by steam distillation, boiled with dilute hydrochloric acid, washed until neutral and dried. There are obtained 80 parts of a tetra-anthrimide which probably corresponds to the formula:

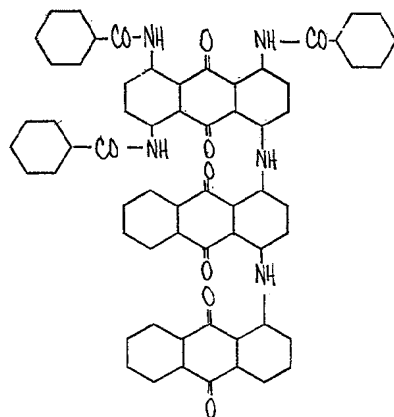


(b) When this product is melted with five times its amount of aluminium trichloride in pyridine at 140 to 145° C. for 2 hours and worked up with dilute hydrochloric acid, a dyestuff is obtained which dyes cotton in greenish-grey shades. The dyestuff obtained is the tricarbazole which may be derived from the structural formula given above.

#### EXAMPLE 5

(a) 30 Parts 1,4,5 - tribenzoylamino - 8 - chloro-anthraquinone, 23.5 parts 4 - amino-1,1' - dianthrimide, 400 parts naphthalene, 5

- 5 parts sodium carbonate and 2 parts cuprous chloride are heated together for 8 hours until the naphthalene reaches boiling point. The melt is stirred until it has cooled to 120° C, then diluted with 400 parts chlorobenzene and the precipitated reaction product is filtered off with suction at 100° C and freed from the organic solvent by steam distillation. There are obtained 47 parts of the trianthrimide of the formula:



This dissolves in concentrated sulphuric acid with a dirty olive-green colour. The colour of the flakes in water is violet, with a black tint.

- (b) 40 Parts of this anthrimide are stirred in an aluminium chloride/pyridine melt at 140° C for one hour and the melt is worked up in the usual manner with an excess of a dilute lye. 39.5 Parts of a dyestuff are obtained, which dyes cotton from a khaki-coloured vat in a full blue-grey shade; it is chemically the bis-carbazole derivative which may be derived from the structural formula given above.

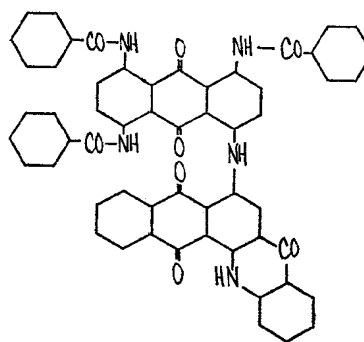
#### EXAMPLE 6

- When, in Example 5, an equal amount of 4 - amino - 1,1' - dianthrimide - carbazole is used, instead of 4 - amino - 1,1' - dianthrimide, a corresponding anthrimide - monocarbazole is obtained, which dissolves in concentrated sulphuric acid with a yellow-brown colour and dyes cotton from a red-brown vat in an olive-green shade.

#### EXAMPLE 7

- (a) 30 Parts of 1,4,5-tribenzoylamino-8-chloro - anthraquinone, 18 parts 2 - amino-3,4-phthaloylacridone, 400 parts naphthalene, 4 parts sodium carbonate, 2 parts cuprous chloride and a trace of copper powder are heated together for 5 hours until the naphthalene reaches boiling point. The melt is diluted with 400 parts chlorobenzene, the product is filtered off with suction, steam distilled, after the addition of hydrochloric acid,

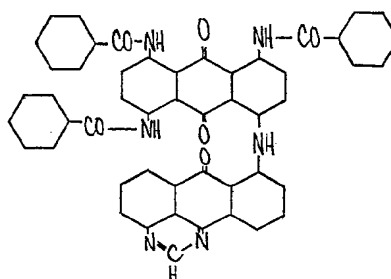
again filtered off with suction, washed until neutral and dried. There are obtained 39 parts of the anthrimide of the formula:



This dissolves in concentrated sulphuric acid with a brown colour. The colour of the flakes in water is olive-green. (b) When this product is carbazolised as described in Example 1 (b), a dyestuff is obtained which dyes cotton from a red-brown vat in a full reddish-grey shade.

#### EXAMPLE 8

- (a) 50 Parts 1,4,5 - tribenzoylamino - 8 - chloro - anthraquinone, 22.5 parts 5 - amino-anthrapyrimidine, 13.5 parts sodium acetate, 2 parts cuprous chloride and some copper oleate are heated in 500 parts naphthalene for 3 hours to boiling temperature. The reaction product already begins to precipitate after a short time. The melt is stirred until it has cooled to 120° C, then diluted with 500 parts pyridine and the product is filtered off with suction at 90° C, washed with pyridine, water, hot dilute hydrochloric acid and again with water. There are obtained 55 parts of the anthrimide of the formula:

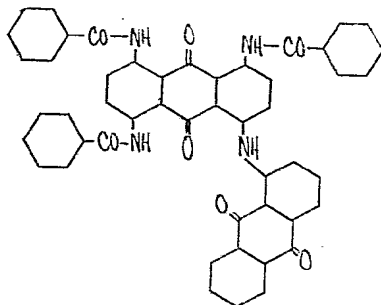


This dissolves in concentrated sulphuric acid with a greenish-khaki colour. The colour of the flakes in water is blue. (b) When this product is carbazolised as described in Example 1 (b), a dyestuff is obtained which dyes cotton from a brown vat in a black-brown shade.

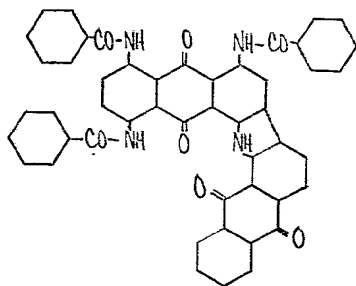
## WHAT WE CLAIM IS:—

1. 1,4,5 - triacylamino -  $\alpha,\alpha'$  - anthrimides and their corresponding 1,4,5 - triacyl carbazolisation products.

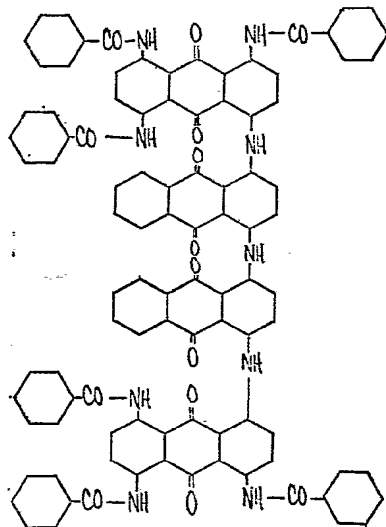
5 2. The compound of the formula



3. The compound of the formula

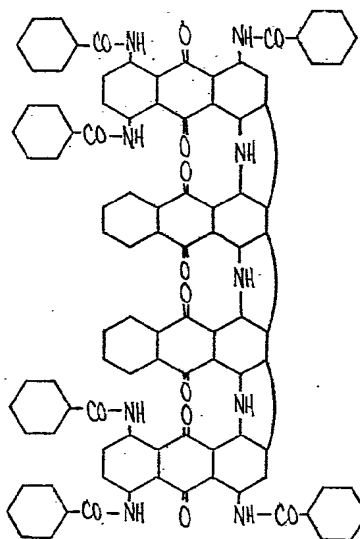


4. The compound of the formula

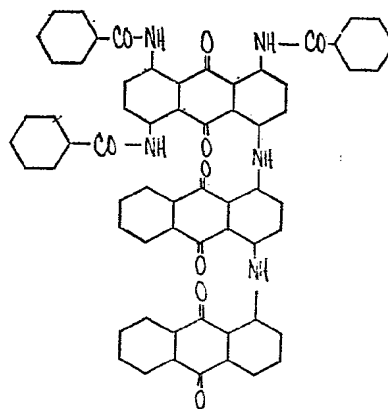


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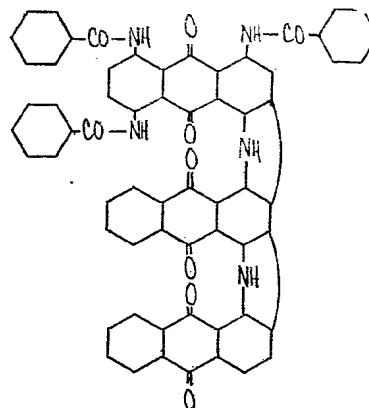
5. The compound of the formula



6. The compound of the formula

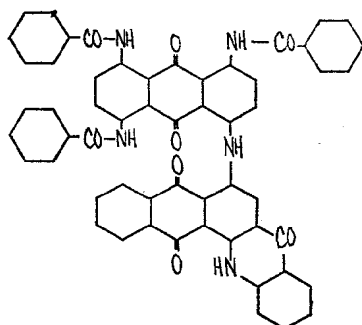


7. The compound of the formula

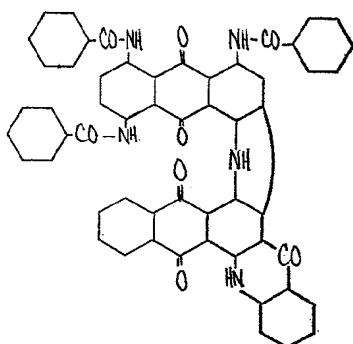


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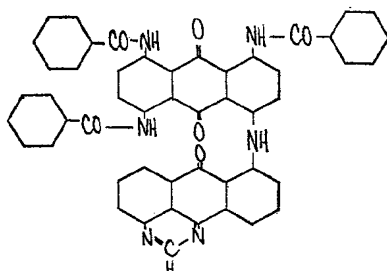
## 8. The compound of the formula



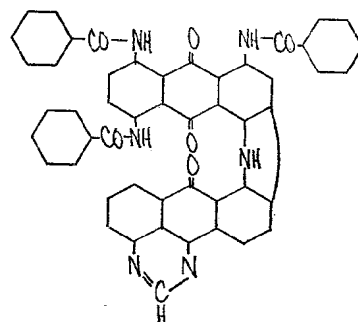
## 9. The compound of the formula



## 5 10. The compound of the formula



## 11. The compound of the formula



12. Process for the production of compounds according to claim 1, wherein a 1,4,5 - triacylamino - 8 - chloro - anthraquinone is reacted with an amine of the anthraquinone series to give the corresponding anthrimide which is, if desired, condensed in the presence of a condensing agent to give the corresponding anthraquinone-carbazole.

13. Process according to claim 12, wherein the reaction with the amine is carried out by boiling the reaction components in a high-boiling organic solvent.

14. Process according to claim 12 or 13, wherein the reaction with the amine is carried out in the presence of an acid-binding agent.

15. Process according to any of claims 12 to 14, wherein the reaction with the amine is carried out in the presence of a catalyst.

16. Process according to claim 12, wherein the condensing agent is aluminium chloride alone or in combination with sodium chloride, a tertiary organic base, ammonia or sulphurous acid.

17. Process for the production of compounds according to claim 1, substantially as hereinbefore described and exemplified.

19. Compounds of the general formula given in claim 1, whenever produced by the process according to any of claims 12 to 18.

20. Vegetable fibre materials, whenever dyed or printed with a dyestuff according to any of claims 1 to 11 and 19.

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